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Patent Application No. 2002-367487 filed by ASAHI
ORGANIC CHEMICALS INDUSTRY CO., LTD. dated December 19,
2002, and certify that the following is a true
translation to the best of my knowledge and belief.

Signature of Translator


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5 [LIST OF DOCUMENTS ATTACHED]

[DOCUMENT NAME] Specification 1

[DOCUMENT NAME] Drawings 1

[DOCUMENT NAME] Abstract 1

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10 [NEED FOR PROOF] Need

[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION] PROCESS FOR PRODUCTION OF
PHENOLIC NOVOLAK

[CLAIMS]

5 [Claim 1] A process for production of a phenolic
novolak, comprising:

a step of conducting a heterogeneous reaction of a
phenol and an aldehyde in the presence of a phosphoric
acid and an unreactive oxygen-containing organic
10 solvent as a reaction cosolvent.

[Claim 2] The process for production of a phenolic
novolak according to claim 1, wherein the phosphoric
acid is 25 parts by mass or more per 100 parts by mass
of the phenol.

15 [Claim 3] The process for production of a phenolic
novolak according to any of claims 1 to 2, wherein the
reaction cosolvent is at least one element selected
from the group consisting of an alcohol, a
polyalcohol-based ether, a cyclic ether, a
20 polyalcohol-based ester, a ketone and a sulfoxide.

[DETAILED EXPLANATION OF THE INVENTION]

[0 0 0 1]

[TECHNICAL FIELD TO WHICH AN INVENTION PERTAINS]

The present invention relates to a process for
25 production of a phenolic novolak, and more
particularly to a production process capable of
producing a phenolic novolak having the contents of a
monomeric phenol and a dimeric phenol and a degree of
dispersion controlled in high yield.

30 [0 0 0 2]

[PRIOR ART]

Conventionally, the phenolic novolak is generally produced by switching from a homogeneous reaction of a phenol and an aldehyde in the presence of an acid

5 catalyst to a heterogeneous reaction starting from an emulsification phenomenon, further pursuing the reaction, checking the production of an initial condensate having a desired degree of condensation before terminating the condensation reaction, and

10 conducting the reduction of low-molecular-weight components and dehydration in the initial condensate by vacuum concentration. And, the phenolic novolak has relatively favorable electric properties and also excels in heat resistance and flame retardance.

15 Therefore, it is extensively used as a base resin for an epoxy resin which is used for, for example, electric and electronic materials, semiconductor sealers and the like required to have remarkable electric properties or a curing agent for epoxy resins,
20 and also used as a binder for laminated plates, forming materials, mold materials, and the like.

[0 0 0 3]

But, when the conventional phenolic novolak was used for the electric and electronic materials,
25 semiconductor sealers or the like, the resin contained a monomeric phenol and a dimeric phenol in a large amount, so that there were various problems resulting from the monomeric phenol such as environmental pollution because of volatilization of the monomeric
30 phenol involving an odor, and the like, and various

problems resulting from the dimeric phenol such as a degradation in production efficiency because of falling of the dimeric phenol, which were sublimated to deposit on the side and ceiling of the apparatus when a photoresist was baked, onto the substrate such as glass for liquid crystal display, and a degradation in crosslinking density of a cured resin substance affecting on the heat resistance, and the like. Because the molecular weight distribution was broad, there were also disadvantages that the molten resin had a high viscosity and poor moldability.

[0 0 0 4]

For example, as a method for reduction of the monomeric phenol and dimeric phenol contained in the above phenolic resin, there is proposed a method of removing low-molecular weight components by blowing in inert gas or vapor to condense a novolak-based condensate at 150°C to 210°C after the condensation reaction is completed (patent document 1). This method has a reliable effect of decreasing the monomeric phenol and dimeric phenol but has a disadvantage that their removal lowers the yield of the resin.

[0 0 0 5]

[PATENT DOCUMENT 1]

Japanese Patent Publication No. Hei 7-91352

[0 0 0 6]

[PROBLEM TO BE SOLVED BY THE INVENTION]

The present invention has been made in view of the above circumstances and provides a process for

production capable of producing a phenolic novolak with the contents of a monomeric phenol and a dimeric phenol and a degree of dispersion controlled in high yield.

5 [0 0 0 7]

[MEANS FOR SOLVING THE PROBLEM]

The present inventors have made a devoted study in order to remedy the above-described problems and achieved the present invention by finding that a
10 phenolic novolak with the contents of a monomeric phenol and a dimeric phenol and a degree of dispersion controlled can be obtained in high yield by a condensation reaction of a phenol and an aldehyde in a phase separation condition, i.e. a heterogeneous
15 condition, including a phosphoric acid and a specified organic solvent.

[0 0 0 8]

The process for production of a phenolic novolak of the present invention comprises a step of
20 conducting a heterogeneous reaction of a phenol with an aldehyde in the presence of a phosphoric acid, preferably 25 parts by mass or more of the phosphoric acid per 100 parts by mass of the phenol, and an unreactive oxygen-containing organic solvent as a
25 reaction cosolvent.

[0 0 0 9]

[MODE FOR CARRYING OUT THE INVENTION]

A process for production of the phenolic novolak according to the present invention has a step which
30 requires a phenol and an aldehyde as raw materials, a

phosphoric acid as an acid catalyst, and an unreactive oxygen-containing organic solvent as a reaction cosolvent, stirs to mix them in a two-phase separated state by, mechanical stirring, ultrasonic wave or the like, and pursues a reaction between the phenol and the aldehyde in a cloudy heterogeneous reaction system with the two phases mixed to synthesize a condensate .

5 [0 0 1 0]

Then, for example, a water-insoluble organic solvent ,e.g., methyl ethyl ketone, methyl isobutyl ketone or the like, is added and mixed to dissolve the condensate, and the mixture is left standing to separate into the organic phase and the water phase. Then, the water phase is removed for recovering the phosphoric acid and the reaction cosolvent, while the organic phase is washed with hot water to remove the phosphoric acid, and the water-insoluble organic solvent is completely removed by vacuum distillation to obtain the novolak resin.

10 [0 0 1 1]

Examples of the phenol used as the raw material are phenol, cresol, xylenol, butylphenol, phenylphenol and the like.

15 [0 0 1 2]

Meanwhile, examples of the aldehyde are formic aldehyde, formalin, paraformaldehyde, trioxane, acetic aldehyde, paraaldehyde, propionaldehyde and the like. Among them, the paraformaldehyde is desirable in view of a degree of dispersion.

20 [0 0 1 3]

Those raw materials are not limited to the exemplified ones and can be used alone or as a combination of two or more of them.

[0 0 1 4]

5 A compounding mole ratio (F/P) of the phenol (P) and the aldehyde (F) is preferably 0.41 to 1.0, and more preferably 0.50 to 0.90. If it is less than 0.40, there is a possibility that the effect of improving the yield is degraded. If it is more than 1.00, there
10 is a possibility that the molecular weight distribution is broad.

[0 0 1 5]

 The phosphoric acid used as the reaction catalyst plays an important role to form a place for a
15 phase separation reaction (a heterogeneous reaction) with the phenol and the aldehyde. Examples of the phosphoric acid are polyphosphoric acid such as metaphosphoric acid, pyrophosphoric acid, orthophosphoric acid, triphosphoric acid, or
20 tetraphosphoric acid, anhydrous phosphoric acid, the mixture of them, and the like. A solution of orthophosphoric acid, which is low cost and easy to get, e.g., 89% by mass phosphoric acid or 75% by mass phosphoric acid, is desirable.

25 [0 0 1 6]

 The compounding amount of the phosphoric acid is not limited, but is preferably 25 parts by mass or more per 100 parts by mass of the phenol, and its upper limit is not limited. In view of reaction volumetric
30 efficiency and safety and the like, it is preferably

40 to 100 parts by mass, per 100 parts by mass of the phenol. Where 70 parts by mass or more of phosphoric acid is used, it is desirable to secure safety by suppressing heat generation in the early stage of reaction by split-charging to the reaction system.

[0 0 1 7]

The unreactive oxygen-containing organic solvent as the reaction cosolvent plays a very important role to promote the phase separation reaction. As the reaction cosolvent, it is desirable to use at least one member selected from a group consisting of an alcohol, a polyalcohol-based ether, a cyclic ether, a polyalcohol-based ester, a ketone and a sulfoxide.

[0 0 1 8]

Examples of the alcohol are monohydric alcohol such as methanol, ethanol or propanol, dihydric alcohol such as butanediol, pentanediol, hexanediol, ethylene glycol, propylene glycol, trimethylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol or polyethylene glycol, trihydric alcohol such as glycerin, and the like.

[0 0 1 9]

Examples of the polyalcohol-based ether are ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, ethylene glycol monopentyl ether, ethylene glycol dimethyl ether, ethylene glycol ethylmethyl ether, ethylene glycol mono phenyl ether and the like.

[0 0 2 0]

Examples of the cyclic ether are 1,3-dioxane,
1,4-dioxane and the like, examples of the polyalcohol-
based ether are glycol esters such as ethylene glycol
acetate, examples of the ketones are acetone, methyl
5 ethyl ketone, methyl isobutyl ketone and the like, and
examples of the sulfoxide are dimethyl sulfoxide,
diethyl sulfoxide and the like.

[0 0 2 1]

Among them, ethylene glycol monomethyl ether,
10 polyethylene glycol and 1,4-dioxane are particularly
desirable.

[0 0 2 2]

The reaction cosolvents are not limited to the
above-described examples but solid types can also be
15 used if they have the above-described properties and
are in a state of liquid at the time of the reaction.
And, they can be used alone or as a combination of two
or more. The reaction cosolvent is not limited to a
particular blending amount but used in 5 parts by mass
20 or more, and preferably 10 to 200 parts by mass, per
100 parts by mass of phenol.

[0 0 2 3]

An amount of water in the reaction system has an
effect on a phase separation effect and a production
25 efficiency but is generally 40% or less according to
the mass standard. If the amount of water exceeds 40%,
there is a possibility that the production efficiency
decreases.

[0 0 2 4]

30 A reaction temperature between the phenol and the

aldehyde is important to develop the phase separation effect, and generally 40°C or more, preferably 80°C to a reflux temperature, and more preferably a reflux temperature. The reaction time is variable depending on the reaction temperature, blending ratio of raw materials, blending amount of phosphoric acid and the like but generally about 1 to 30 hours. As a reaction environment, it is general to have normal pressure, but the reaction may be made under pressure or under a reduced pressure if the heterogeneous reaction which is a feature of the present invention is maintained.

[0 0 2 5]

When the process for production of the present invention is used, the following phenolic novolaks are generally obtained in the compounding mole ratio (F/P) of an aldehyde (F) and a phenol (P).

[0 0 2 6]

When the compounding mole ratio (F/P) is in a range of 0.80 mol or more and 1.00 mol or less, phenolic novolak can be produced in that a total content of a monomeric phenol and a dimeric phenol is 10% or less, and preferably 5% or less according to the measurement made by the GPC area method, and the degree of dispersion (Mw/Mn) of the weight-average molecular weight (Mw) and the number-average molecular weight (Mn) is 1.1 to 3.0, preferably 1.5 to 2.0, according to GPC measurement. Molecular weight (Mw) of this resin is preferably 600 to 4500, more preferably 900 to 3500.

[0 0 2 7]

When the compounding mole ratio (F/P) is in a range of 0.40 or more and less than 0.80, phenolic novolak can be produced in that a monomeric phenol content is 3% or less, preferably 1% or less, and a dimeric phenol content is 10% to 75%, preferably 20% to 60% when measured by the GPC area method. This resin has a molecular weight (Mw) in 300 to 1000, preferably 330 to 900, and a degree of dispersion (Mw/Mn) of the weight-average molecular weight (Mw) and the number-average molecular weight (Mn) in 1.1 to 1.8, preferably 1.2 to 1.7, according to GPC measurement.

[0 0 2 8]

[OPERATION]

It is not necessarily clear why the novolak resin is obtained in good yield with the contents of the monomeric phenol and dimeric phenol and the degree of dispersion controlled according to the process for production of the invention but it is presumed as follows.

[0 0 2 9]

In the heterogeneous reaction system in a cloudy state that the phase A (the phenol as the main ingredient) and the phase B (the phosphoric acid, the aldehyde and a reaction cosolvent as the main ingredients) are mixed, the low-molecular-weight component which removed to the phase B from the phase A by the dissolution promoting action of the reaction cosolvent in the phase B, reacts promptly with the aldehyde under the catalyzing conditions of a lot of

phosphoric acid, and grows as a condensate which cannot dissolve in the phase B, and moves to the phase A having a little phosphoric acid and a little aldehyde, and the further growth of the condensate is suppressed or stopped, so that it is prevented from being of high molecular weight. Thus, the process of the invention applies a two-liquid phase interface reaction having a mechanism of suppressing the resinification of the phenol in the water phase and the resin from being of high molecular weight in the organic phase, so that it is assumed that the resin having the contents of the monomeric phenol and dimeric phenol and a degree of dispersion (Mw/Mn) controlled is produced, and the yield is considerably improved.

[0 0 3 0]

[EXAMPLES]

Then, the present invention will be described in further detail in examples but not limited to such examples. Every "parts" and "%" described in the Examples mean "parts by mass " and "% by mass "

[0 0 3 1]

The properties of the produced novolak resin were measured by the following testing methods.

[0 0 3 2]

(1) Degree of dispersion

Weight-average molecular weight (Mw) and number-average molecular weight (Mn) in terms of the standard polystyrene calibration were determined by Tosoh Corporation's gel permeation chromatography 8020

series build-up system (column: G2000Hx1+G4000Hx1,
detector: UV 254 nm, carrier: tetrahydrofuran 1 ml/min,
column temperature: 38°C), and a degree of dispersion
(Mw/Mn) was calculated.

5 [0 0 3 3]

(2) Contents (%) of monomeric phenol and dimeric
phenol

Areas of a monomeric phenol and a dimeric phenol
to the entire area of the molecular weight
10 distribution obtained by GPC were measured by an area
method indicating in percentage.

[0 0 3 4]

(3) Softening point

According to the Ring-and-Ball method described
15 in JIS-K6910, a ring-and-ball type automatic softening
point measuring apparatus ASP-MGK2 produced by MEITECH
Company, Ltd. was used for measurement.

[0 0 3 5]

(4) Melt viscosity

20 Measured by a cone plate viscometer (CONE PLATE
VISCOMETER MODEL CV-1 produced by TOA Industry Inc.).

[0 0 3 6]

<Example 1>

Into a reaction vessel provided with a
25 thermometer, a stirring device and a condenser, 193
parts of phenol (P), 57 parts of 92% paraform (F)
(F/P=0.85), 116 parts of 89% phosphoric acid (60%/P),
96.5 parts of ethylene glycol (50%/P) were charged
and gradually raised to a reflux temperature in a
30 cloudy condition (two-phase mixture) formed by

stirring for mixing, and at the same temperature, a condensation reaction was conducted for ten hours, then the reaction was stopped.

【0037】

5 Then, methyl isobutyl ketone was added to dissolve the condensate while stirring for mixing, the stirring for mixing was stopped, the content was moved into a separating flask and left standing to separate into a methyl isobutyl ketone solution layer (upper
10 layer) and an aqueous phosphoric acid solution layer (lower layer). Then, the aqueous phosphoric acid solution layer was removed, the methyl isobutyl ketone solution was washed with water several times to remove phosphoric acid, the content was returned into the
15 reaction vessel, and the methyl isobutyl ketone was completely removed by vacuum distillation to obtain 213.5 parts of the novolak resin.

【0038】

20 The obtained resin was measured for its properties according to the testing method described above. The results are shown in Table 1. A GPC chart of the obtained resin is shown in Fig. 1.

【0039】

<Examples 2 to 7,9,10>

25 Phenolic Novolaks were obtained in the same manner as in Example 1 except that the reaction conditions were changed as shown in Table 1. The obtained phenolic Novolaks were measured for its properties according to the same method. The results
30 are shown in Table 1. In Table 1, "N.D." indicates no

detection.

【0 0 4 0】

<Example 8>

Phenolic Novolak was obtained in the same manner
5 as in Example 1 except that into a pressure-resistant
reaction vessel provided with a thermometer, a
stirring device and a condenser, 193 parts of
orthocresol, 43.7 parts of 92% paraformaldehyde, 116
parts of 89% phosphoric acid, 29 parts of methanol
10 were charged and raised to 150 °C in a cloudy
condition (two-phase mixture) formed by stirring for
mixing, and at the same temperature, a condensation
reaction was conducted for one hour (the internal
pressure was 0.08 to 0.10 MPa), then the condensation
15 reaction was stopped.

【0 0 4 1】

The obtained resin was measured for its
properties according to the testing method described
above.

[0 0 4 2]

[Table 1]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10
Raw material	Phenol (parts)	193	193	193	193	193	0	0	0	193
	Orthocresol (parts)	0	0	0	0	0	193	193	0	0
	Metacresol (parts)	0	0	0	0	0	0	0	193	0
	92% Paraform (parts)	57	57	57	57	0	49	49	49	33.5
	37%Formalin (parts)	0	0	0	0	142	0	0	0	0
	Compounding ratio(F/P)	0.85	0.85	0.85	0.85	0.85	0.75	0.75	0.75	0.5
Catalyst	89% Phosphoric acid solution (parts)	116	116	116	116	116	116	116	116	116
	Oxalic acid (parts)	0	0	0	0	0	0	0	0	0
	Compounding amount of phosphoric acid (%/P)	60	60	60	60	60	53.4	53.4	53.4	60
Cosolvent	Name	Ethylene glycol	1,4-Dioxane	1,4-Butanediol	Methanol	1,4-Dioxane	Ethylene glycol	Methanol	Ethylene glycol	1,4-Dioxane
	Usage (%/P)	50	50	50	5.9	50	20	15	15	10
Reaction time (hour)										
Monomeric phenol(%)										
Dimeric phenol(%)										
Number-average molecular weight(Mn)										
Weight-average molecular weight(Mw)										
Degree of dispersion (Mw/Mn)										
Melt viscosity (Pa·s/150°C)										
Softening point(°C)										
Yield(%/P)										

【 0 0 4 3 】

<Comparative Example 1>

Into a reaction vessel provided with a thermometer, a stirring device and a condenser, 193 parts of phenol (P), 142 parts of 37% formalin (F) (F/P=0.85) and 0.97 parts of oxalic acid (0.5%/P) were charged and gradually raised to a reflux temperature (98 to 102°C) and, at the same temperature, a condensation reaction was conducted for six hours, and concentration was conducted under a reduced pressure to obtain 199g of a phenolic novolak (yield 103%/P). The obtained phenolic Novolak was measured for its properties according to the same method as Example 1. The results are shown in Table 2. A GPC chart of the obtained phenolic novolak is shown in Fig. 2.

【 0 0 4 4 】

<Comparative Examples 2 to 3>

Novolak resins were obtained in the same manner as in Comparative Example 1 except that the reaction conditions were changed as shown in Table 2. The obtained phenolic Novolaks were measured for its properties according to the same method. The results are shown in Table 2.

【 0 0 4 5 】

<Comparative Examples 4>

Novolak resin was obtained in the same manner as in Example 1 except that the reaction conditions were changed as shown in Table 2. The obtained phenolic Novolak was measured for its properties according to the same method. The results are shown in Table 2.

[0 0 4 6]

[Table 2]

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Reaction conditions	Phenol (parts)	193	193	193	193
	Orthocresol (parts)	0	0	0	0
	Metacresol (parts)	0	0	0	0
	Raw material	0	0	0	0
	92% Paraform (parts)	142	130	83	142
	37%Formalin (parts)	0.85	0.78	0.5	0.85
	Compounding ratio(F/P)	0	0	0	116
	89% Phosphoric acid solution (parts)	0.97	0.97	0.97	0
	Oxalic acid (parts)	—	—	—	60
	Compounding amount of phosphoric acid (%/P)	—	—	—	—
Catalyst	Name	—	—	—	—
	Usage (%/P)	0	0	0	0
	Reaction time (hour)	6	6	8	15
Properties	Monomeric phenol(%)	2.6	1.2	0.5	0.3
	Dimeric phenol(%)	9.4	11.2	26.4	5.5
	Number-average molecular weight(Mn)	888	873	432	741
	Weight-average molecular weight(Mw)	4606	2165	651	1469
	Degree of dispersion (Mw/Mn)	5.19	3.2	1.5	1.98
	Melt viscosity (Pa·s/150°C)	13.0	4.2	0.12	1.8
	Softening point(°C)	115	108.8	68.4	106.3
	Yield(%/P)	103	97	75	109.8

[0 0 4 7]

[ADVANTAGEOUS EFFECT OF THE INVENTION]

According to the present invention, the phenolic novolak with the contents of the monomeric phenol and a dimeric phenol controlled, and having the narrow degree of dispersion can be obtained easily and with low cost, and the production efficiency can be improved, by the phosphoric acid phase separation reaction in the presence of a phosphoric acid and a reaction cosolvent.

[0 0 4 8]

The phenolic novolak obtained by the process for production of the present invention is useful as, for example, a base resin for epoxy resins, a curing agent for epoxy resins, and also as an environmental responsive binder for IC sealers, laminated plates, casting materials, forming materials and the like, because the monomeric phenol is very little and the dimeric phenol is also decreased considerably as compared with the conventional resins.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[Fig. 1]

A GPC chart of the novolak resin obtained in Example 1.

[Fig. 2]

A GPC chart of the novolak resin obtained in Comparative Example 1.

[EXPLANATION OF THE MARKS]

1 a monomeric phenol

2 a dimeric phenol

[NAME OF DOCUMENT] ABSTRACT

[ABSTRACT]

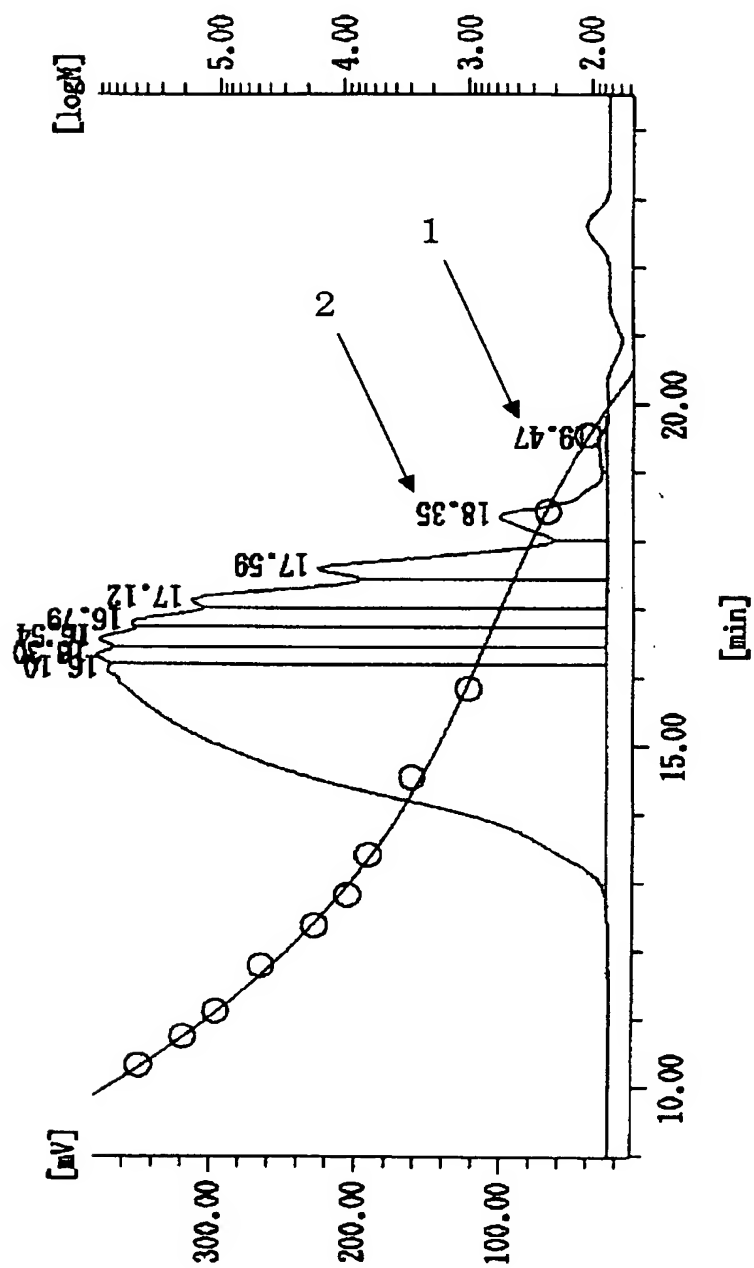
[PROBLEM] The present invention provides a process for production capable of producing a phenolic novolak
5 with the contents of a monomeric phenol and a dimeric phenol and a degree of dispersion controlled in high yield.

[MEANS FOR SOLVING] A process for production of a phenolic novolak having a step of conducting a
10 heterogeneous reaction of a phenol and an aldehyde in the presence of a phosphoric acid and an unreactive oxygen-containing organic solvent as a reaction cosolvent.

[SELECTED DRAWING] None

[NAME OF DOCUMENT] DRAWINGS

[Fig.1]



[Fig. 2]

